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Los Alamos NATIONAL LABORATORY

RADIOCHEMICAL SEPARATION AND SPECTROMETRIC ANALYSES OF AMERICIUM AND PLUTONIUM, Thesis Prospectus

Rebecca Mueller

February 11, 2022

LA-UR

Welcome

- Committee Members
  - Dr. Ralf Sudowe (chair)
  - Dr. John Auxier, II
  - Dr. Thomas Johnson
  - Dr. Sherrod Maxwell
  - Dr. Alexander Brandl
  - Dr. Thomas Borch

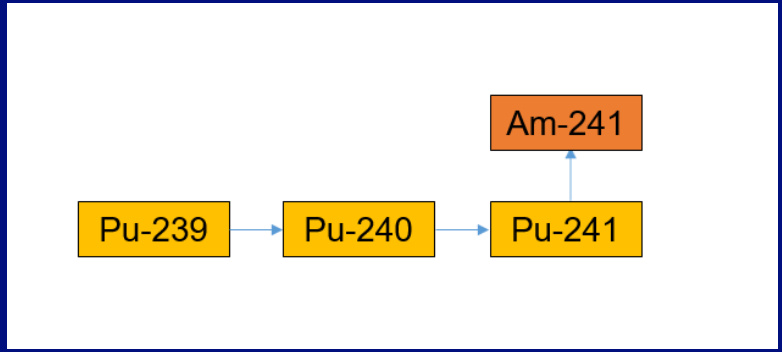
- Special thanks
  - Other Sudowite graduate students
  - Kim Bonilla
  - Dr. Stephanie Velardo

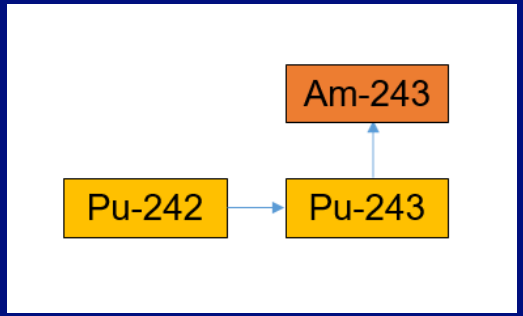
Outline

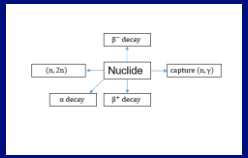
- Why now? (Current Views)
- History
- Experimental & Results
- Issues/Future Work

Why now? An Intro to Am

- Discovered in 1944 by Seaborg, et al. at the University of Chicago (schema to right)
- Importance
  - Am-241 is a by-product of Pu-239 production and decay, and is removed during Pu purification
  - Very useful due to its low cost, convenience, spectral purity and half-life
  - Largest use as a low-energy gamma-ray source







W. H. Runde & W. W. Schultz, “Chemistry of the Actinides and Transactinides”, Springer, 2006

Why now? An Intro to Am (cont.)

Image: EPA, “Radionuclide Basics: Americium-241”

- Uses
  - Fire-detection applications
  - Important in energy security as it can be paired with Be to make neutron sources for well-logging
  - Gauging thickness, density, and radiographic measurements
  - Production of Cm-242, for the start-up of nuclear reactors

W. H. Runde & W. W. Schultz, “Chemistry of the Actinides and Transactinides”, Springer, 2006

Why now? Why Am and Pu?

- C-AAC performs analyses for programmatic support at TA-55
  - Certain analysis are performed to measure concentrations of Pu and Am-241 in process solutions
  - Solutions contain high levels of Pu (e.g., g/L) and Am-241, with significant amounts of stable isotopes
- Pu-238, 239, 240, 242 contribute alpha activity.
  - Am-241, alpha emitter, overlaps with Pu-238 emission
  - Pu-239, a major component of weapons grade Pu, has a half-life of 24,000 yrs, in contrast, Am-241 has a shorter half-life of 400 yrs. This creates the situation where a small mass fraction of Am-241 can contribute a majority of the overall alpha activity.
    - For example 5.0% Am-241 by mass contributes 74.4% of the overall alpha activity.
- Currently two techniques are employed, depending on the level of Am-241 in the sample.

Why now? Separation Schemes

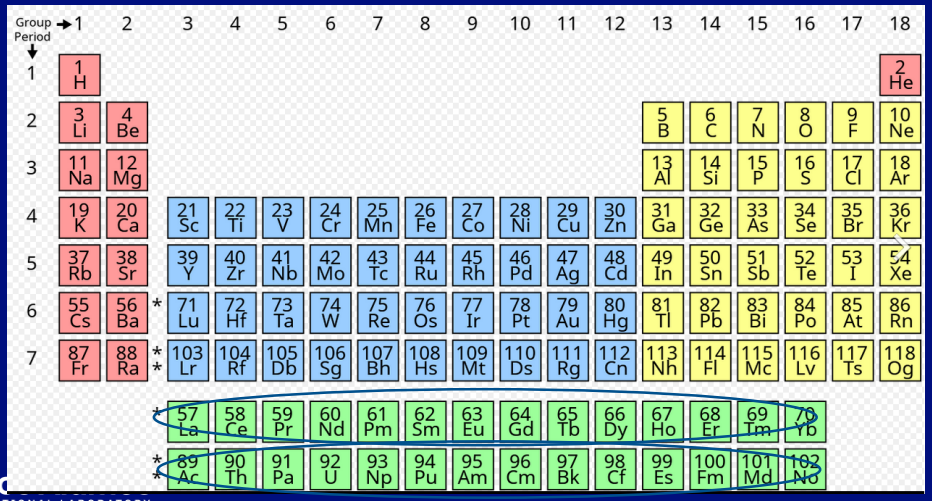
- Less Am-241 (Am-241 α activity < 90% overall α activity):
  - Dilute sample and divide into two portions
  - One portion, place on glass slip, to be counted in gas-proportional counter to determine total alpha
  - Second portion counted on an NaI(Tl) counter to determine Am-241 (59 keV gamma)
- More Am-241 (Am-241 α activity > 90 % overall α activity):
  - Liquid-liquid separation to separate Pu and Am-241
  - Counts are done of the two resulting fractions
  - Avoids the situation where the difference between large alpha counts and NaI(Tl) count is dominated by relative uncertainties of both counts
- Liquid-Liquid separation generates a waste stream with limited disposition options.
  - Flammability issues with the organic phase (TTA/xylene)

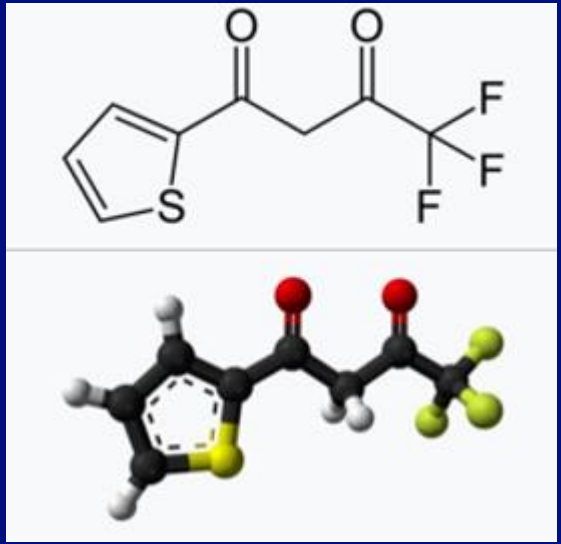
Outline

- Why now?
- History (A Review of the Separation)
- Experimental & Results
- Issues/Future Work

History

- Thenoyltrifluoroacetone (TTA) has been used for the separation of rare earth metals since the late 1940s (1)
- TTA use for extracting actinides via liquid-liquid extraction has been used since the 1940s/1950s (2)





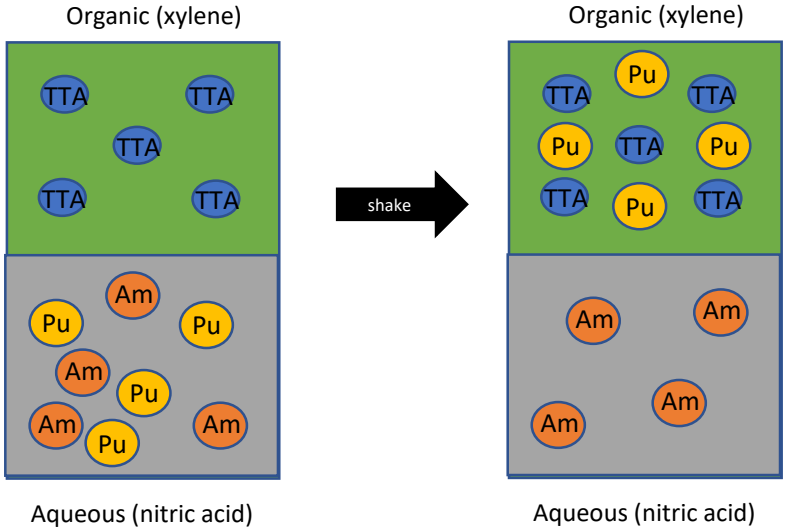
(1) *Anal. Chem.* Vol. 29, No. 12, pp. 1767-1770 (1957)
(2) JACS, Vol. 76, pp. 1982-1984 (1954)

History

- Solvent extraction
  - Distribution of a chemical species between two immiscible phases—typically aqueous and organic
  - Wide range of available reagent concentrations
  - Rapid and specialized separations
  - Distribution ratio given by $D^{SE} = \frac{c_{org}}{c_{aq}}$
  - Separation factor given by $SF_{AB} = \frac{D_A}{D_B}$

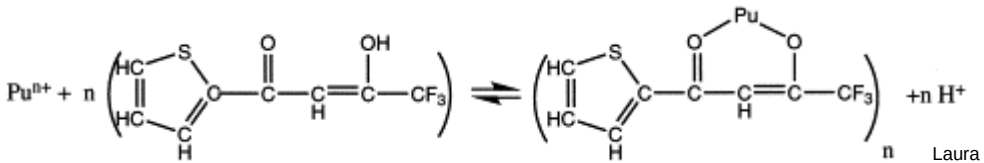
Modern Applications, edited by Frank Rösch, De Gruyter, Inc., 2016. ProQuest Ebook Central, https://ebookcentral.proquest.com/lib/alamos/detail.action?docID=4644589.
Friedlander, Gerhart, J.W. Kennedy, E.S. Macias, J.M. Miller. Nuclear and Radiochemistry, 3rd Ed. 1981.

History



- TTA is selective for +4 oxidation state Pu
- Was originally done in benzene, known carcinogen

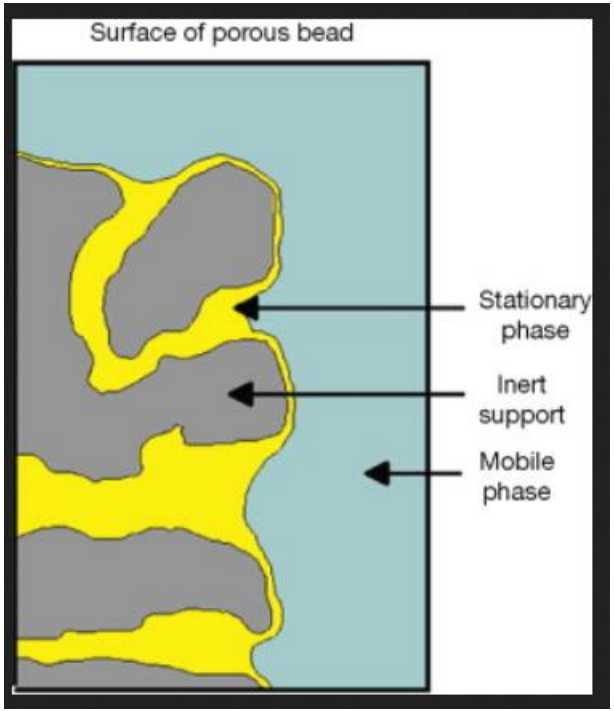
$$D_w = \frac{Activity_{organic\ phase}}{Activity_{aqueous\ phase}}$$



Laura Gagliardi, et al.
Chemical Physics,
Vol:252, Issues 1–2, 2000,pp. 47-55

History

- Extraction Chromatography
  - Extractant material mounted on inert substrate
  - Aqueous solution passed through column material, typically inorganic acids or mineral acids
  - Effective for the separation of metal ions
  - Advantages of good selectiveness of extractants and multistages of chromatography



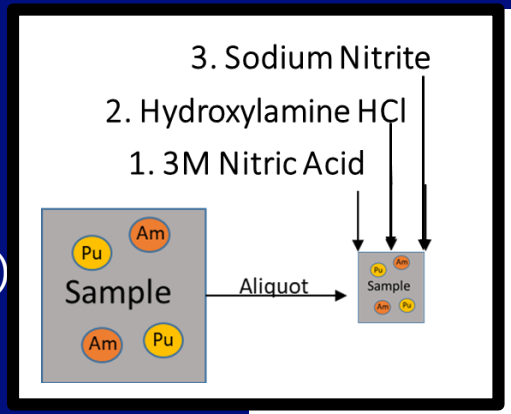
Conceptual section through an extraction chromatography (EXC) porous bead impregnated with the stationary, organic extracting phase, and the surrounding aqueous mobile phase.
E.P. Horwitz, http://www.eichrom.com/products/extraction.cfm.

Outline

- Why now?
- History
- Experimental (Procedure) & Results
- Issues/Future Work

Experimental

1. Adjust pH of solution
2. Add NH_2OH HCl for Pu(III)
3. 10 minutes in hot water bath, if needed
    1. Allow to cool (if hot water bath was used)
1. Add 2 M $NaNO_2$ for Pu(IV)
2. Add 0.5 mL TTA in xylene
3. Shake
4. Transfer aliquot to cover slip
5. Count when dry



LA-UR—85-3444 DE86 000801

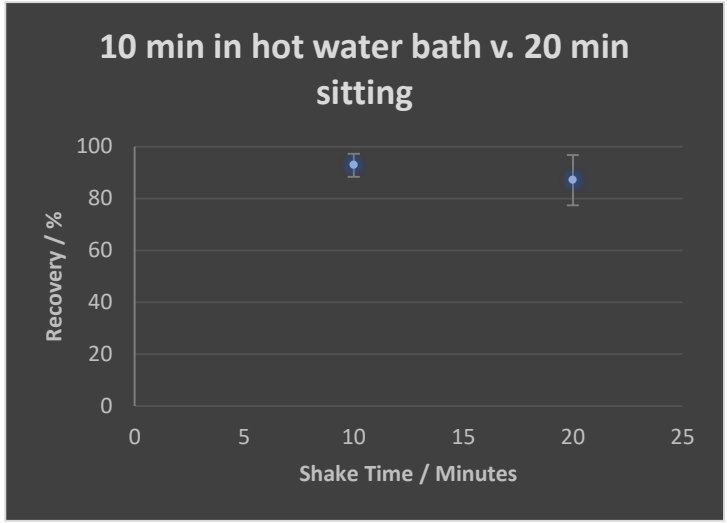
Nelson S. Stalnaker & TJ Beugelsdijk

Results

TABLE IV

EFFECT OF TEMPERATURE ON RATE CONSTANTS

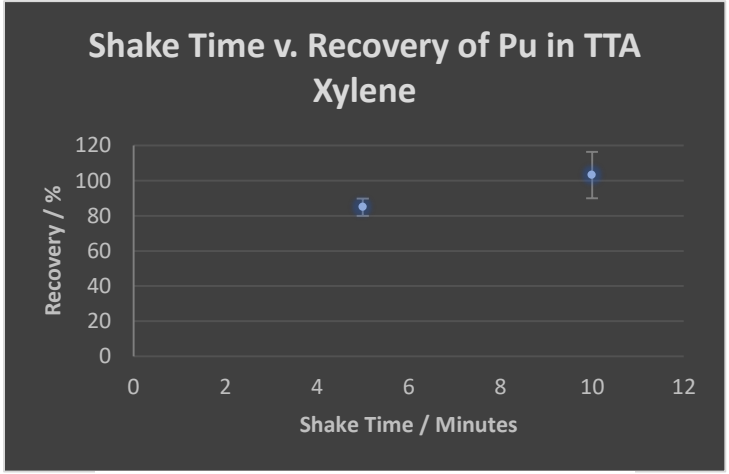
Temperature, °C	k_1, mol $l.^{-1}$ sec^{-1}	k_2, sec^{-1}	$k_3(K_1)$
25	7.04 ±1.14	48.2 ± 9.1	2.14 ±0.49
35	26.6 ±3.5	135. ±19.	2.10 ±0.28
40	38.1 ±2.9	347. ±32.	2.49 ±0.11
45	68.6 ±7.0	720. ±67.	2.82 ±0.16

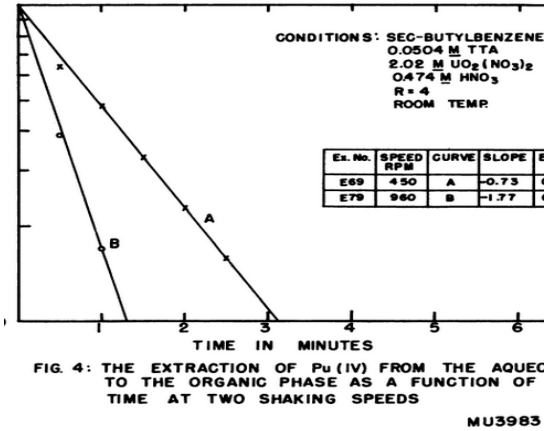


Barney, G S. KINETICS AND MECHANISM OF PLUTONIUM(IV) REDUCTION BY HYDROXYLAMINE.. United States: N. p., 1971. Web. doi:10.2172/4591822.

Results

- Rate limiting step is transfer of chelated Pu across aqueous-organic boundary layer
- Increase in stirring speed does lead to faster extraction
- Amount of stirring when hand shaking does agree with this (vortex mixing preferred)



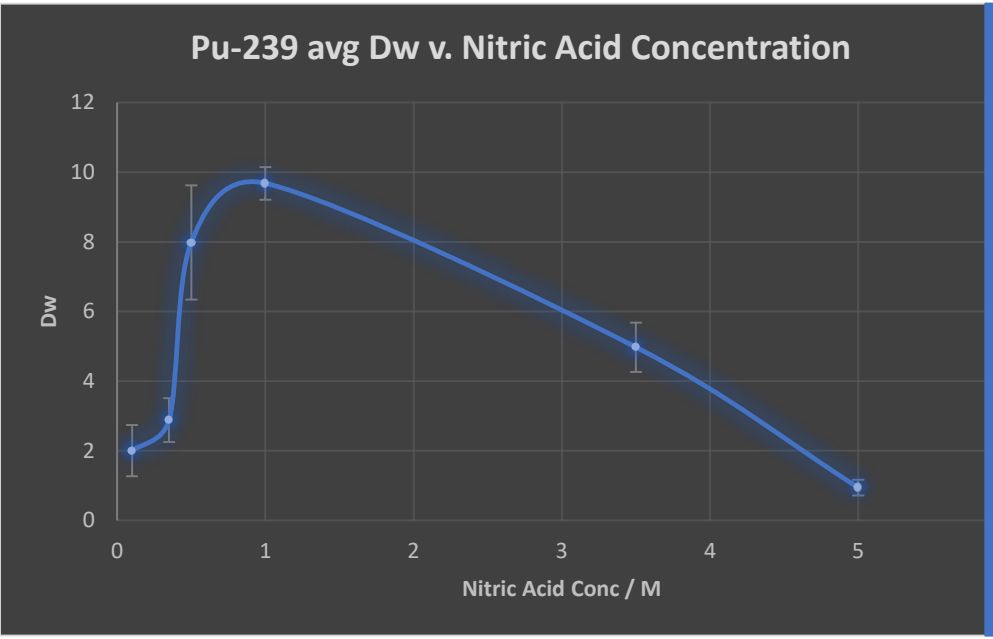


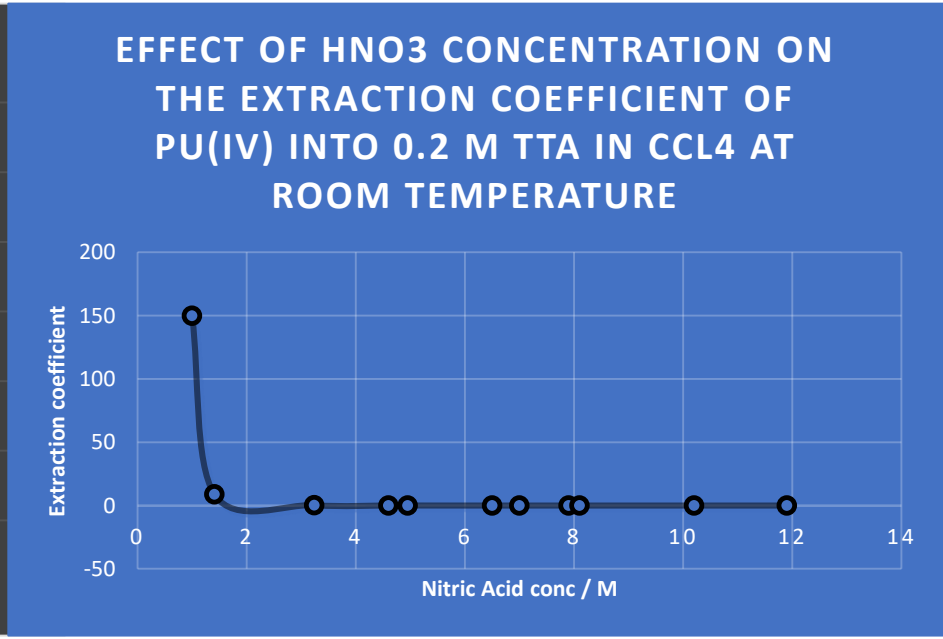
Barney, G S. *KINETICS AND MECHANISM OF PLUTONIUM(IV) REDUCTION BY HYDROXYLAMINE.*. United States: N. p., 1971. Web. doi:10.2172/4591822.

Experimental

1. Control redox state of Pu-239 with hydroxylamine hydrochloride and sodium nitrite
2. Add 50 Bq Pu-239 to each sample
3. Contact 2 mL aqueous (of various acid concentrations) with 2 mL 0.5 M TTA in xylene
4. Allow to settle and remove 1 mL from each phase
5. Add scintillation cocktail and count via LSC

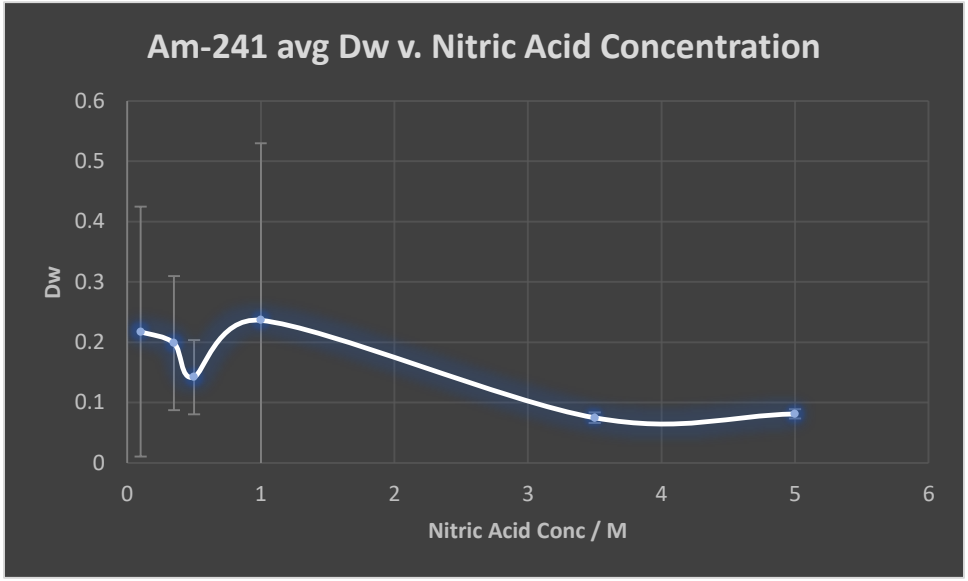
Results



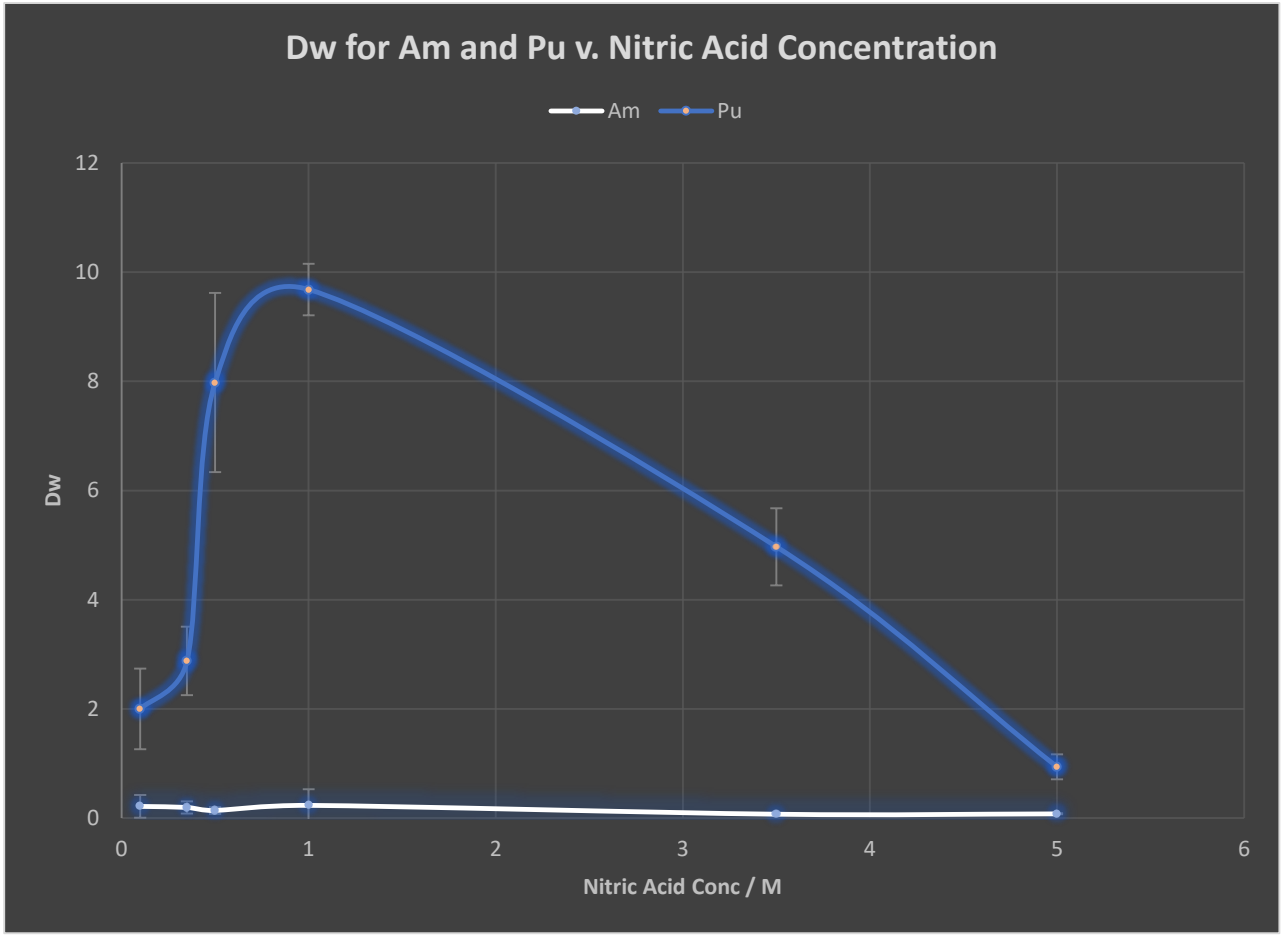


Plutonium Handbook, 1968

Results

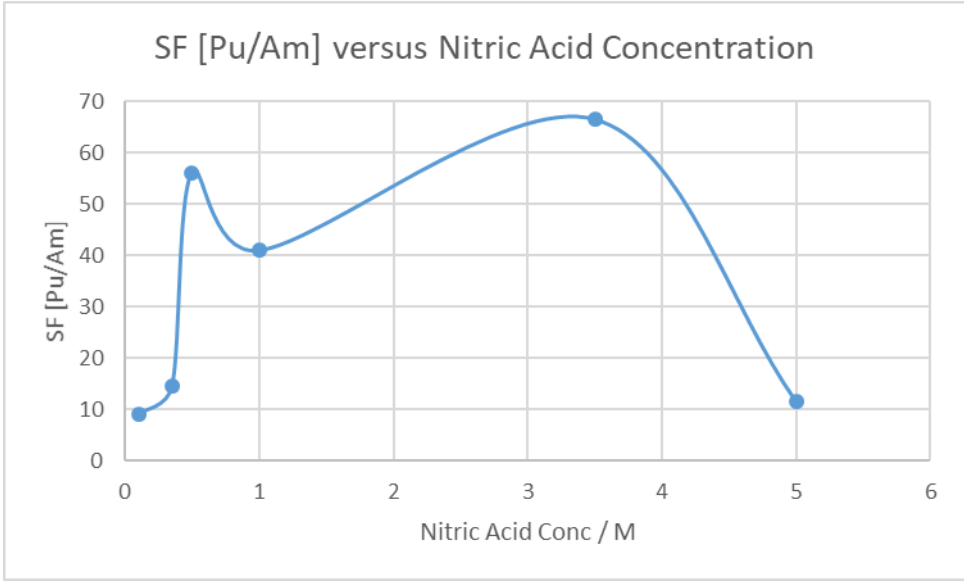

Am-241 avg Dw v. Nitric Acid Concentration
Dw
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
5
6
Nitric Acid Conc / M

Results


Dw for Am and Pu v. Nitric Acid Concentration
Am
Pu
Dw
Nitric Acid Conc / M
0
2
4
6
8
10
12
0
1
2
3
4
5
6

Separation Factors

- Optimal separation is at 1M nitric acid
- Separation factors are higher at 0.5 and 3.5 M
- Likely due to the very very small Dw of Am at these concentrations



Nitric Acid Concentration / M	Dw: Am(standard deviation)	Dw: Pu (standard deviation)	SF
0.1	0.22(0.21)	2(0.74)	9.2
0.35	0.20(0.11)	2.88(0.63)	14.51
0.5	0.14(0.06)	7.98(1.64)	56.2
1	0.24(0.29)	9.68(0.47)	40.97
3.5	0.07(0.01)	4.97(0.71)	66.49
5	0.08(0.01)	0.94(0.23)	11.6

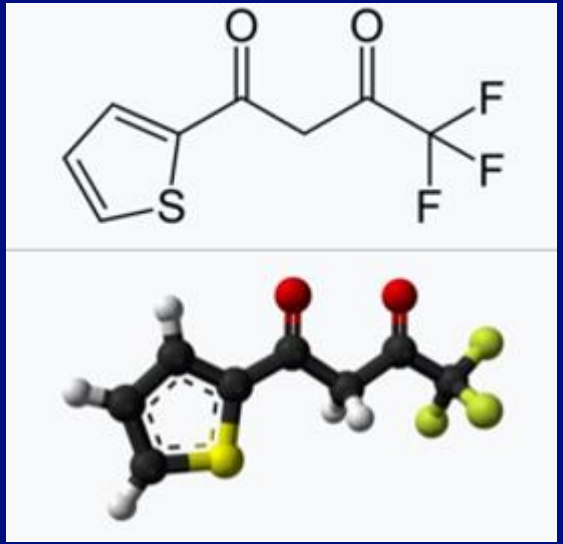
Conclusion

1. 1 M Nitric Acid worked best
2. TTA-xylene separation has separation factor >9 for Pu relative to Am at all concentrations tested
3. Effective separation

HOWEVER!....

Issues and Further Work

1. TTA has 3 fluorides
2. Low atomic numbers have higher cross-sections for (α, n) reaction
3. Fluorine undergoes (α, n) reaction leading to large neutron dose of the waste drum
4. Potential neutron dose to workers should be avoided when ever possible

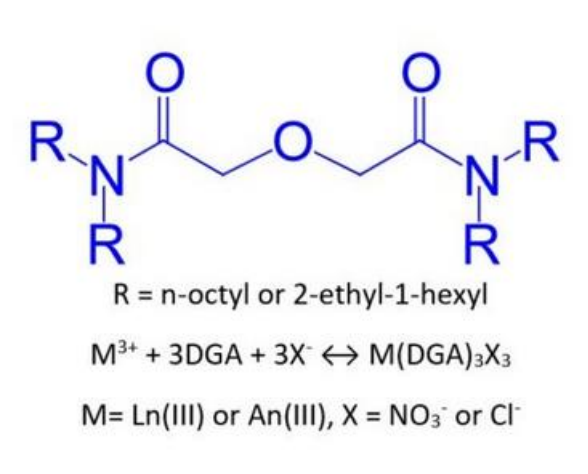


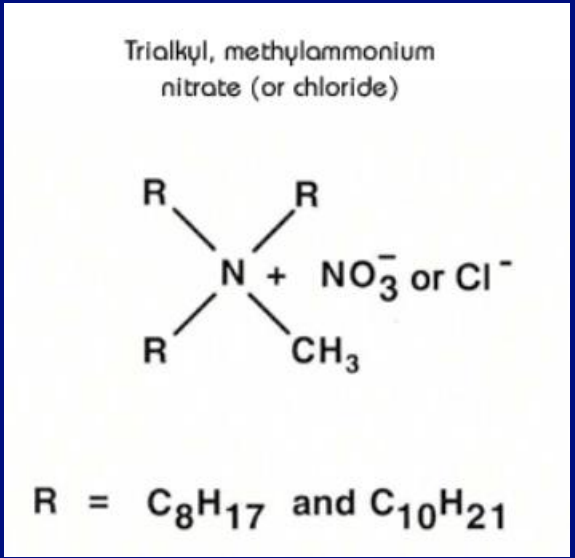
Issues and Further Work

1. Xylene is a problematic waste constituent
2. Other solvents with TTA
    1. AmeriClear
    2. HistoClear
    3. Dodecane
    4. 1,3-diethylbenzene

Column Separation

- When Am is major constituent, use separation medium that selects for tetravalent ions, like TEVA (trialkyl, methylammonium nitrate or chloride)
- When Pu is major constituent, use separation medium that selects for trivalent ions, like DGA



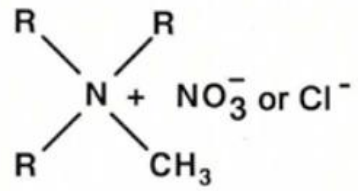


Eichrom website, DGA and TEVA Resin pages

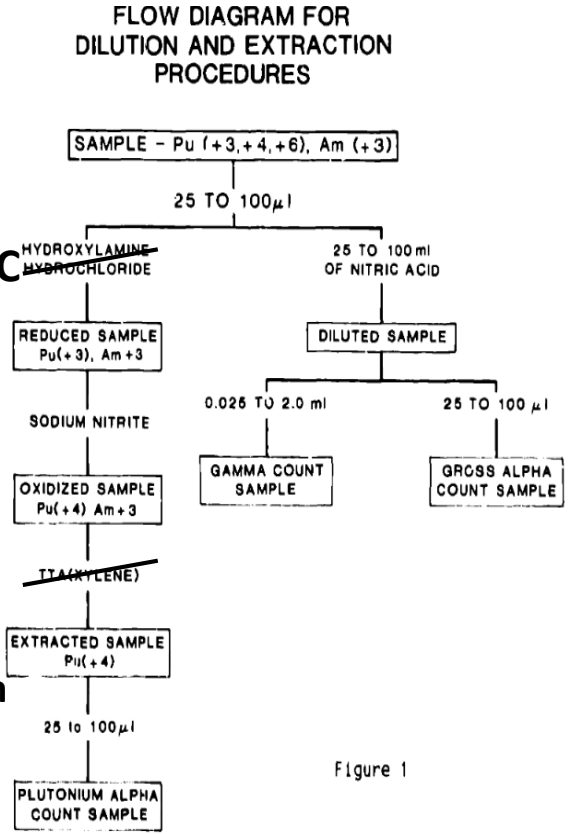
Column Separation

- TEVA extractant structure shown (below)
- Experimental flow diagram shown (right)
- Control redox state of Pu with ascorbic acid and sodium nitrite

Trialkyl, methylammonium nitrate (or chloride)



R = C_8H_{17} and $C_{10}H_{21}$



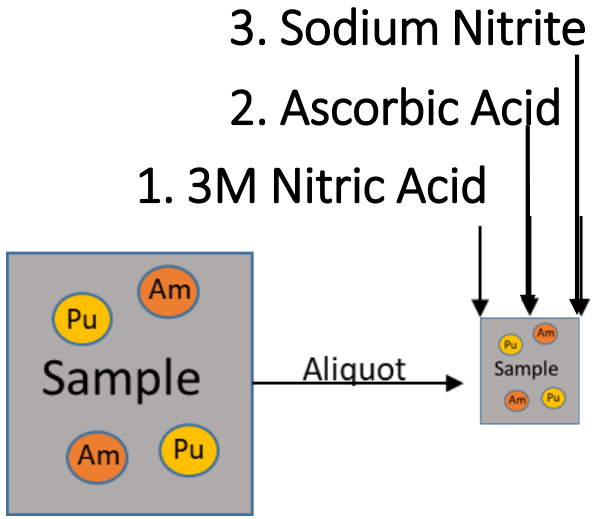
ASCORBIC ACID

TEVA column separation

Eichrom website, TEVA Resin page

LA-UR—85-3444 DE86 000801
Nelson S. Stalnaker & TJ Beugelsdijk

TEVA Column Extraction



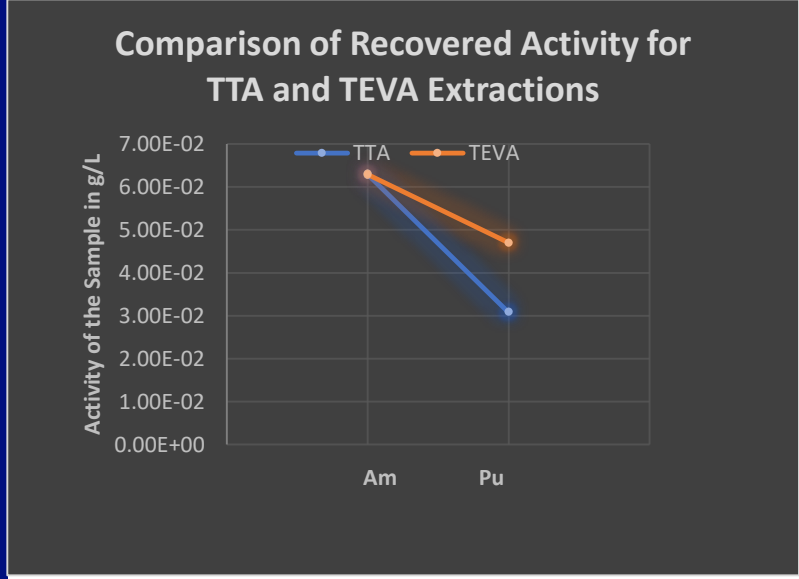
5. Add 3mL 0.02M HNO3-0.005M HF
4. Rinse column with 3M Nitric Acid x2
3. Rinse sample tube with 3M Nitric Acid
2. Load Sample Pu & Am onto Column
1. Nitric Acid precondition

TEVA Column

1. Collection vessel for disposal
2. Collect Am in solution, not retained
3. Collection vessel for disposal
4. Collection vessel for disposal
5. Collect Pu in new vial, plate fraction for α counting

Results: Initial TTA/TEVA Comparison

- Same sample, two analyses
- Am determined concentration was equal in both
- Pu determined concentration was higher with TEVA



Outline

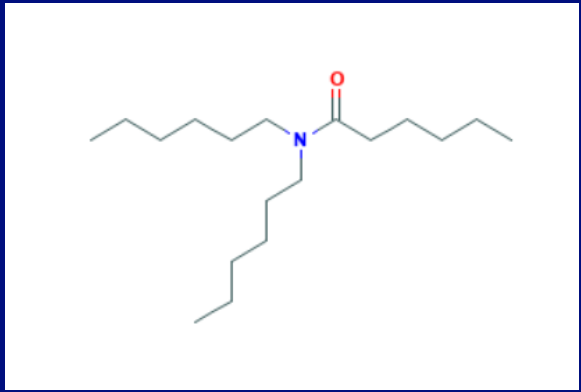
- History
- Why now?
- Experimental
- Results
- Issues/Future Work (Moving Forward)

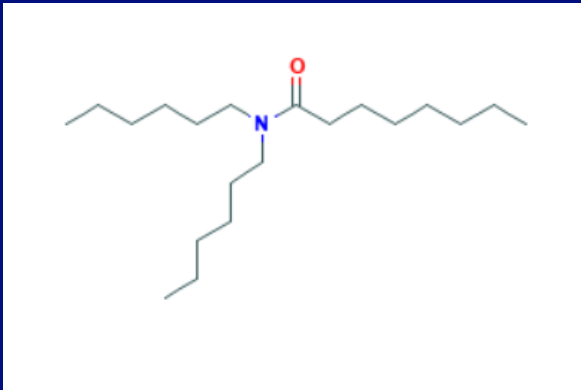
Issues and Further Work

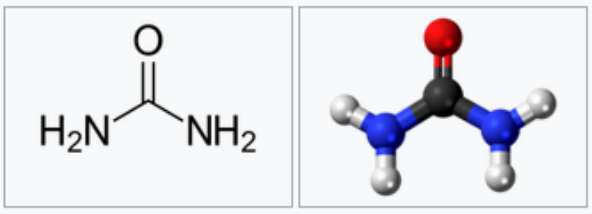
1. Xylene is a problematic waste constituent
   - Other solvents???
2. Fluorine undergoes (α, n) reaction leading to large neutron dose of the waste drum
3. PuTTA complex on UV-Vis (next slide)
4. Other extractants
   - Dihexyl Hexanamide (DHHA)
   - Dihexyl Octanamide (DHOA)
   - Tetra- or tri-alkylcarbamides

Issues and Further Work: Other Extractants

- Dihexyl Hexanamide (DHHA) (left)
- Dihexyl Octanamide (DHOA) (middle)
- Tetra- or tri-alkylcarbamides (basic carbamide structure shown right)







Other Extractants, cont.

Figure 1. Distribution ratios as functions of acidity for hexavalent actinides Pu(VI) ( ), Np(VI) ( ), and U(VI) ( ) using 1 M monoamide/Exxsol D60. Lines are plotted as a visual guide

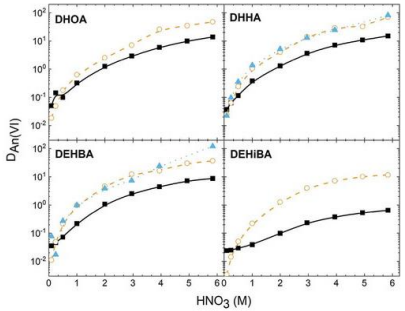


Figure 4. Distribution ratios as functions of acidity for tetravalent actinides Pu(IV) ( ), Np(IV) ( ), and Th(IV) ( ) using 1 M monoamide/Exxsol D60. Lines are plotted as a visual guide

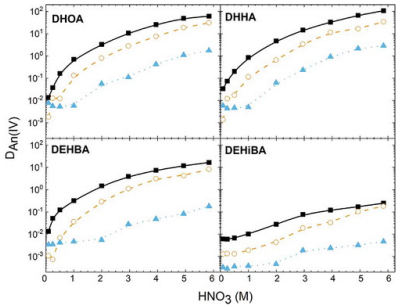


Figure 3. Distribution ratios as functions of acidity for Pa(V) 1 M DEHiBA/dodecane ( )[40] vs. Np(V) DEHiBA ( ), DEHBA ( ), DHOA, ( ), and DHHA ( ) using 1 M monoamide/Exxsol D60. Lines are plotted as a visual guide

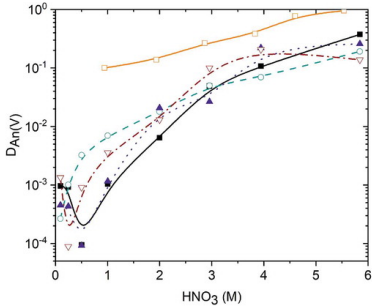
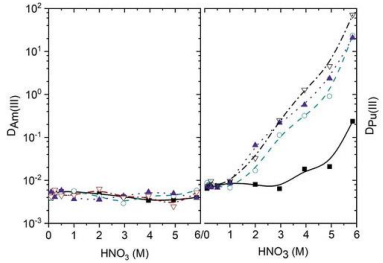


Figure 5. Distribution ratios as functions of acidity for extracting Am(III) (left) and Pu(III) with 0.43 M hydroxylamine (right). DEHiBA ( ), DEHBA ( ), DHOA, ( ), and DHHA ( ) using 1 M monoamide/Exxsol D60. Lines are plotted as a visual guide



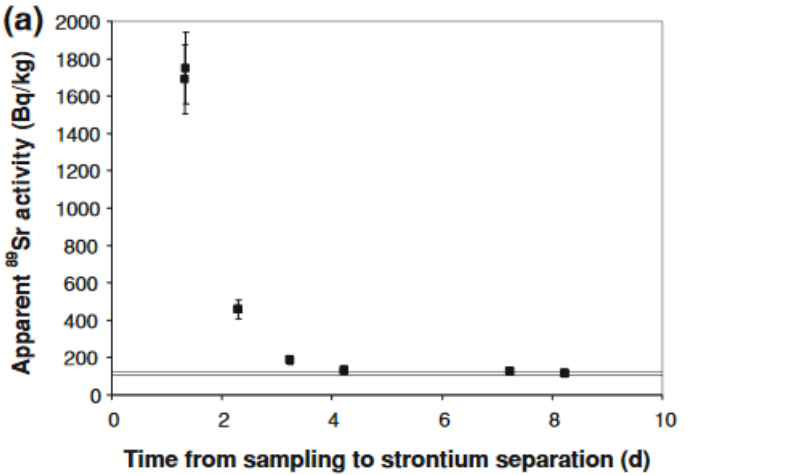
Gogolski, Jarrod M, and Mark P Jensen. "Using N,N-dialkylamides for Neptunium Purification from Other Actinides for Space Applications." *Separation Science and Technology* 56.16 (2021): 2775-788. Web.

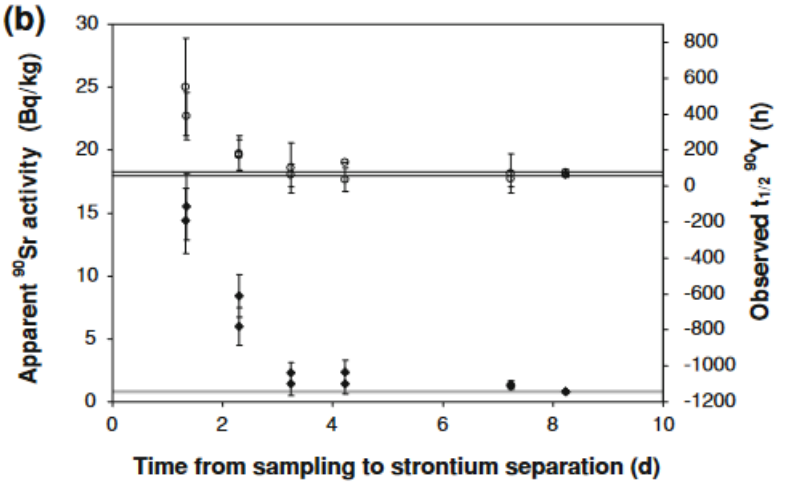
Americium Isotopics

- TIMS: Thermal Ionization Mass Spectroscopy
  - Very Expensive but provides
    - Pu Assay values
    - Am isotopic ratio values (241Am and 243Am)
  - Requires chemical separation similar to previous work
  - Also requires a more lengthy turn-a-round time.

Americium Isotopics

Nuclide	Decay Method	Half-life	Daughter	Emax, β (MeV)	E, α (MeV	E, γ (MeV)
Sr-89	β, γ	**50.5 d**	Y-89	1.5	N/A	N/A
Sr-90	β	**28.8 y**	Y-90	0.546	N/A	N/A
Y-89	STABLE	N/A	N/A	N/A	N/A	N/A
Y-90	β	64.0 h	Zr-90	2.28	N/A	N/A
Am-241	α, γ	**432.6 y**	Np-237	N/A	5.486	0.0595
Am-243	α, γ	**7364 y**	Np-239	N/A	5.275	0.0747
Np-237	α	2.144x10^6 y	Pa-233	N/A	4.788	0.0294
Np-239	β, γ	2.356 d	Pu-239	0.438	N/A	0.1061

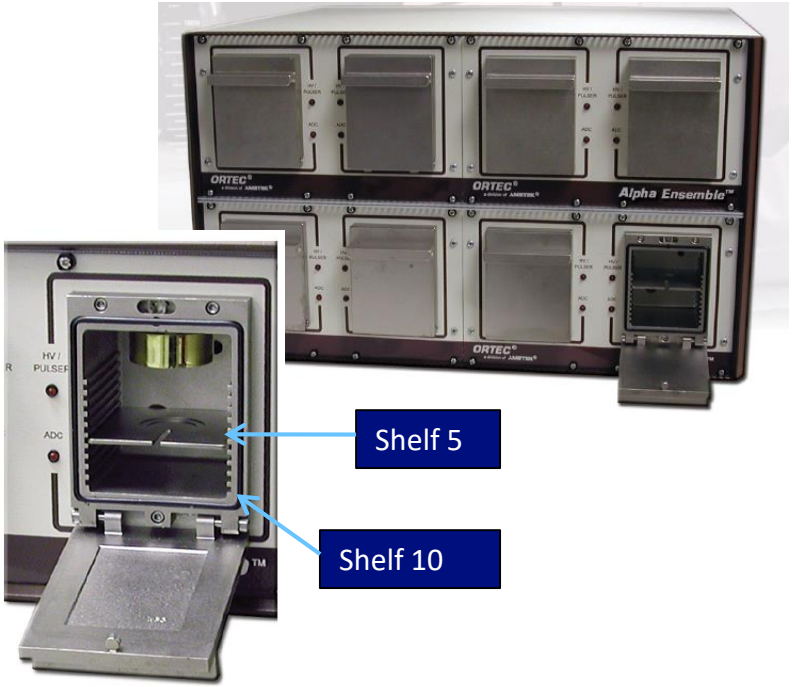




Methodology for determination of 89Sr and 90Sr in radiological emergency: II. Method development and evaluation. Annika Tovedal et al.
J Radioanal Nucl Chem (2009) 282:461–466

Proposed Detection Methods

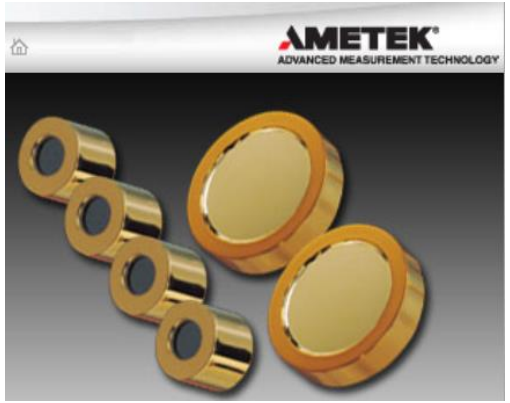
- **ORTEC Octete Spectrometer**



Silicon Detectors

450 mm^2: 17-21 keV, FWHM

50 mm^2: 12-14 keV, FWHM resolution



Photos courtesy of ORTEC, Inc.

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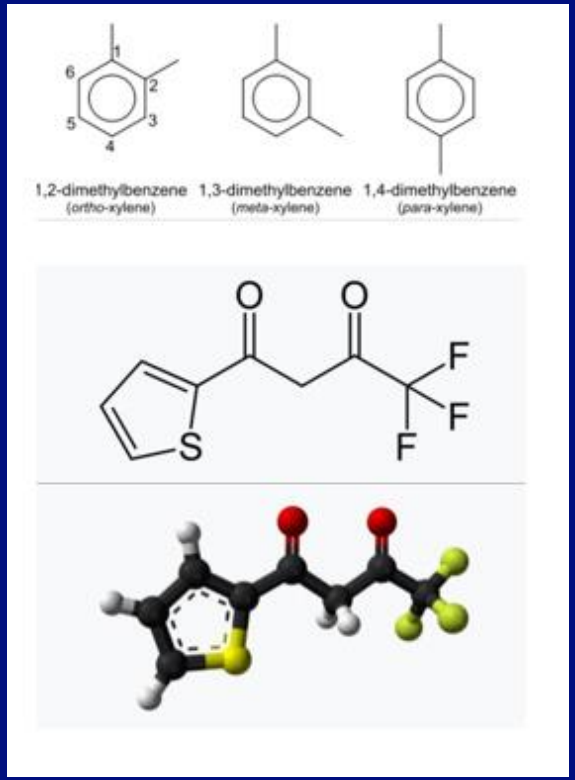
  - Pu Sustainment (NA-10)
  - Seaborg Fellowship

Questions?

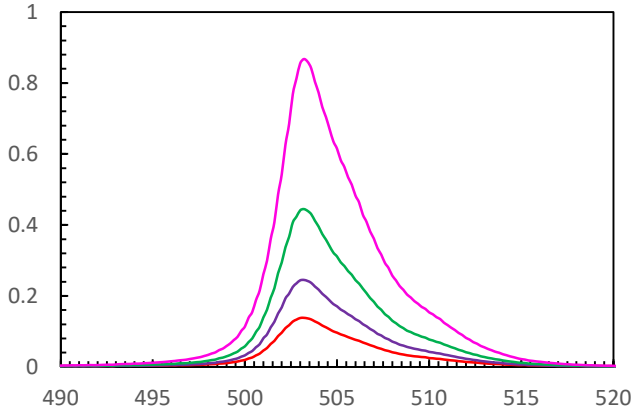
Why now?

- Purity
  - For the majority of these applications, Am purity needs to have > 99% purity (e.g. < 1% Pu and other elements)
  - The feedstock for Am typically doesn't contain other elements so Pu is the major impurity
  - Isotopically needs to be greater than 99% Am-241.
  - Needs to be greater than 95% AmO2 by weight.
- Radiochemical separation?
  - Current is TTA/xylene



UV-Vis Results

- **UV-Vis Spectrometer for Am/Pu Assay**

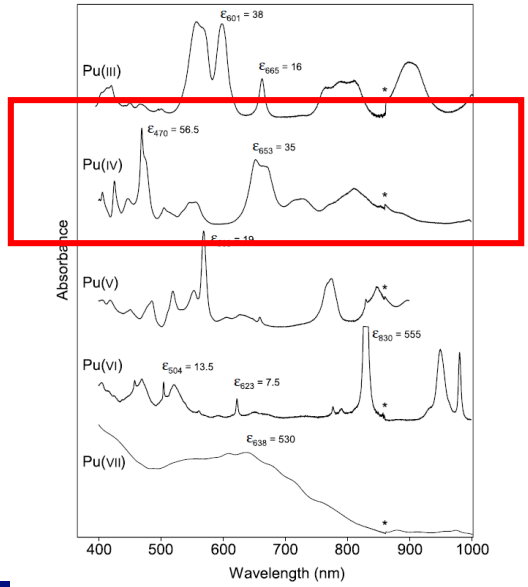


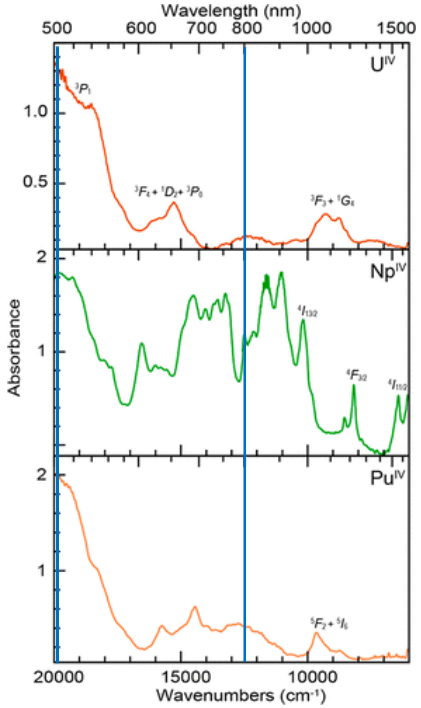
Am Transitions

- ($^7F_0 \rightarrow {}^5L_6$) @ 503 nm
- ($^7F_0 \rightarrow {}^5L_6$) @ 806 nm

Pu^{4+} Transitions

- 470 nm
- 653 nm
- Thus no interference with Am^{3+}





Single-crystal UV–vis–NIR absorption spectra from UIV(TTA)4 (top, red), NpIV(TTA)4 (middle, green), and PuIV(TTA)4 (bottom, orange) crystals.

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